

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 February 2006 (02.02.2006)

PCT

(10) International Publication Number
WO 2006/012046 A3

(51) International Patent Classification:

C07C 51/36 (2006.01) C07F 9/24 (2006.01)
C07C 67/303 (2006.01) C07F 9/6571 (2006.01)
C07C 231/18 (2006.01) C07F 17/00 (2006.01)
C07C 269/06 (2006.01) C07F 17/02 (2006.01)

(21) International Application Number:

PCT/US2005/021376

(22) International Filing Date: 16 June 2005 (16.06.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

10/876,492 25 June 2004 (25.06.2004) US

(71) Applicant: EASTMAN CHEMICAL COMPANY
[US/US]; 100 North Eastman Road, Kingsport, TN 37660
(US).

(72) Inventor: BOAZ, Neil, Warren; 1342 Watauga Street,
Kingsport, TN 37660 (US).

(74) Agent: BLAKE, Michael, J.; P.O. Box 511, Kingsport,
TN 37662-5075 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

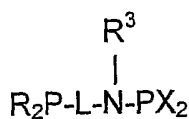
— with international search report

(88) Date of publication of the international search report:

27 April 2006

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PREPARATION OF AMINOPHOSPHINES



(57) Abstract: Disclosed is a process for the preparation of phosphine-aminophosphines that are useful in the formation of catalysts useful in carrying out a wide variety of reactions such as asymmetric hydrogenations, asymmetric reductions, asymmetric hydroborations, asymmetric olefin isomerizations, asymmetric hydrosilations, asymmetric allylations, asymmetric conjugate additions, and asymmetric organometallic additions. The process comprises the steps of

(1) contacting a compound of formula (2): $R_2P-L-NHR^3$ with phosphorus trihalide PX_3 in the presence of an inert, organic solvent and an acid acceptor to produce intermediate compound having formula (3); (2) contacting intermediate compound (3) with a reactant having the formula R^1-M^1 , R^2-M^1 or a mixture thereof.



WO 2006/012046 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/021376

A. CLASSIFICATION OF SUBJECT MATTER
 C07C51/36 C07C67/303 C07C231/18 C07C269/06 C07F9/24
 C07F9/6571 C07F17/00 C07F17/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C07C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, EMBASE, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US 6 939 981 B1 (BOAZ NEIL WARREN) 6 September 2005 (2005-09-06) the whole document	1-15
E	WO 2005/068478 A (STYLACATS LIMITED) 28 July 2005 (2005-07-28) page 3 page 4, line 4 - line 9 page 27 examples 23-32	1-15
E	WO 2005/068477 A (STYLACATS LIMITED) 28 July 2005 (2005-07-28) page 2 page 3, line 7 - line 12 page 22 examples 23-32	1-15
	-/--	

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

<p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*G* document member of the same patent family</p>
--	--

Date of the actual completion of the international search	Date of mailing of the international search report
24 November 2005	06/12/2005

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Elliott, A
--	--------------------------------------

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/021376

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 6 906 213 B1 (BOAZ NEIL WARREN) 14 June 2005 (2005-06-14) the whole document -----	1-15
P,X	US 6 906 212 B1 (BOAZ NEIL WARREN) 14 June 2005 (2005-06-14) the whole document -----	1-15
P,X	ZENG Q-H ET AL: "New unsymmetrical hybrid ferrocenylphosphine-phosphoramidite ligands derived from H8-BINOL for highly efficient Rh-catalyzed enantioselective hydrogenation" TETRAHEDRON: ASYMMETRY, PERGAMON, OXFORD, GB, vol. 16, no. 6, 21 March 2005 (2005-03-21), pages 1233-1238, XP004785968 ISSN: 0957-4166 the whole document -----	1-15
P,X	HU XIANG-PING ET AL: "Practical Rh(I)-catalyzed asymmetric hydrogenation of beta-(acylamino)acrylates using a new unsymmetrical hybrid ferrocenylphosphine-phosphoramidite ligand: crucial influence of an N-H proton in the ligand." ORGANIC LETTERS, vol. 7, no. 3, 3 February 2005 (2005-02-03), pages 419-422, XP009057439 ISSN: 1523-7060 the whole document -----	1-15
P,X	HU XIANG-PING ET AL: "Unsymmetrical hybrid ferrocene-based phosphine-phosphoramidites: a new class of practical ligands for Rh-catalyzed asymmetric hydrogenation." ORGANIC LETTERS, vol. 6, no. 20, 30 September 2004 (2004-09-30), pages 3585-3588, XP009057443 ISSN: 1523-7060 the whole document -----	1-15

-/--

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2005/021376

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JIA X ET AL: "The synthesis of new chiral phosphine-phosphinites, phosphine-phosphoramidite, and phosphine-phosphite ligands and their applications in asymmetric hydrogenation" TETRAHEDRON: ASYMMETRY, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 15, no. 14, 26 July 2004 (2004-07-26), pages 2273-2278, XP004523719 ISSN: 0957-4166 the whole document	1-15
A	WO 03/082885 A (EASTMAN CHEMICAL COMPANY) 9 October 2003 (2003-10-09) the whole document	1-15
A	WO 02/26750 A (EASTMAN CHEMICAL COMPANY) 4 April 2002 (2002-04-04) cited in the application the whole document	1-15
A	NOVIKOVA Z S ET AL: "Synthesis of di(heteroelement)-substituted enamines" JOURNAL OF GENERAL CHEMISTRY OF THE USSR, vol. 59, no. 10, 1989, pages 2134-2135, XP009057434 the whole document	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/021376

Patent document cited in search report	Publication date	Publication date	Patent family member(s)	Publication date
US 6939981	B1	06-09-2005	NONE	
<hr style="border-top: 1px dashed black;"/>				
WO 2005068478	A	28-07-2005	GB 2410950 A	17-08-2005
			GB 2410951 A	17-08-2005
			WO 2005068477 A1	28-07-2005
<hr style="border-top: 1px dashed black;"/>				
WO 2005068477	A	28-07-2005	GB 2410950 A	17-08-2005
			GB 2410951 A	17-08-2005
			WO 2005068478 A1	28-07-2005
<hr style="border-top: 1px dashed black;"/>				
US 6906213	B1	14-06-2005	NONE	
<hr style="border-top: 1px dashed black;"/>				
US 6906212	B1	14-06-2005	NONE	
<hr style="border-top: 1px dashed black;"/>				
WO 03082885	A	09-10-2003	AU 2003225962 A1	13-10-2003
			EP 1487845 A1	22-12-2004
			US 6620954 B1	16-09-2003
<hr style="border-top: 1px dashed black;"/>				
WO 0226750	A	04-04-2002	CN 1612887 A	04-05-2005
			EP 1330464 A2	30-07-2003
			JP 2004509968 T	02-04-2004
			US 2002065417 A1	30-05-2002
<hr style="border-top: 1px dashed black;"/>				